



Nitrogen trace gas emissions from a riparian ecosystem in southern Appalachia

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Abstract

In this paper, we present two years of seasonal nitric oxide (NO), ammonia (NH₃), and nitrous oxide (N₂O) trace gas fluxes measured in a recovering riparian zone with cattle excluded and adjacent riparian zone grazed by cattle. In the recovering riparian zone, average NO, NH₃, and N₂O fluxes were 5.8, 2.0, and 76.7 ng N m⁻² s⁻¹ (1.83, 0.63, and 24.19 kg N ha⁻¹ y⁻¹), respectively. Fluxes in the grazed riparian zone were larger, especially for NO and NH₃, measuring 9.1, 4.3, and 77.6 ng N m⁻² s⁻¹ (2.87, 1.35, and 24.50 kg N ha⁻¹ y⁻¹) for NO, NH₃, and N₂O, respectively. On average, N₂O accounted for greater than 85% of total trace gas flux in both the recovering and grazed riparian zones, though N₂O fluxes were highly variable temporally. In the recovering riparian zone, variability in seasonal average fluxes was explained by variability in soil nitrogen (N) concentrations. Nitric oxide flux was positively correlated with soil ammonium (NH₄⁺) concentration, while N₂O flux was positively correlated with soil nitrate (NO₃⁻) concentration. Ammonia flux was positively correlated with the ratio of NH₄⁺ to NO₃⁻. In the grazed riparian zone, average NH₃ and N₂O fluxes were not correlated with soil temperature, N concentrations, or moisture. This was likely due to high variability in soil microsite conditions related to cattle effects such as compaction and N input. Nitric oxide flux in the grazed riparian zone was positively correlated with soil temperature and NO₃⁻ concentration. Restoration appeared to significantly affect NO flux, which increased ≈600% during the first year following restoration and decreased during the second year to levels encountered at the onset of restoration. By comparing the ratio of total trace gas flux to soil N concentration, we show that the restored riparian zone is likely more efficient than the grazed riparian zone at diverting upper-soil N from the receiving stream to the atmosphere. This is likely due to the recovery of microbiological communities following changes in soil physical characteristics.

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1. Introduction

A riparian zone is the transitional boundary between terrestrial and aquatic ecosystems. Riparian zone functions include sediment and nutrient filtering, stream

organic matter input, and modification of stream physical conditions (e.g., temperature) and wildlife habitat. Thus, this zone heavily influences the function and quality of adjacent aquatic systems. In recent years, the nitrogen (N) over-enrichment of fresh- and salt-water systems has become more widespread on a global scale (Paerl, 1995). Non-point source pollution has become the dominant contributor to N entering these systems and is the most difficult source to manage. Natural and manipulated riparian zones have been shown to effectively reduce the flux of nutrients in ground and surface

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water to aquatic systems (Gilliam et al., 1997). For example, forested and grass buffer strips can reduce N in subsurface waters by 40–100% and 10–60%, respectively (Osborne and Kovacic, 1993). Natural resource managers, farmers, and local citizen-based groups concerned about water pollution are becoming more aware of the value of riparian ecosystems in management of water quality. Thus, the restoration of degraded riparian systems is becoming more widespread. Many regions in the US have set goals to protect riparian zones of thousands of stream miles. We seek to better understand the soil, water, vegetation, and atmospheric processing and exchange of N in pasture and riparian-aquatic systems. Information on the emission of N trace gases from soils along the pasture to stream gradient is a potentially important component of these processes.

Characterization of nitric oxide (NO), nitrous oxide (N_2O), and ammonia (NH_3) emissions from soils provides important information regarding both atmospheric chemistry and soil nutrient and microbial dynamics. While gaseous N fluxes are an important component of N cycling in riparian ecosystems, these gases are also important to atmospheric chemistry on local, regional, and global spatial scales and on temporal scales ranging from hours to decades. For example, N_2O is a greenhouse gas and is also responsible for the destruction of stratospheric ozone (Crutzen, 1970; Ramanaathan et al., 1985). Soils account for approximately 25% (10 Tg N_2O -N y^{-1} ; Tg = 10^{12} g) of global annual N_2O emissions (Warneck, 1988). Nitric oxide plays an integral role in the photochemistry of tropospheric ozone and is also a precursor to atmospheric nitrous and nitric acids (Chameides and Walker, 1973; Galloway and Liens, 1981; Logan, 1983). Global estimates suggest that NO emission from soil contributes approximately 15% (7 Tg NO_x -N y^{-1}) of total nitrogen oxides (NO_x) emissions (44 Tg NO_x -N y^{-1} ; Bouwman, 1990; Lee et al., 1997). Ammonia emissions lead to the formation of ammonium (NH_4^+) aerosol and atmospheric deposition of NH_3 gas and NH_4^+ , which may cumulatively account for a significant fraction of N input to ecosystems downwind of strong NH_3 source regions such as confined animal feeding operations and intensive agriculture. Estimates of NH_3 emissions from grazed pasture and soils under natural vegetation are limited (Langford et al., 1992). Globally, NH_3 emissions from undisturbed ecosystems represent only 4.5% (2.4 Tg NH_3 -N y^{-1}) of total emissions (Bouwman et al., 1997). Synthetic fertilizers and agricultural crops, however, together contribute 24% (12.6 Tg NH_3 -N y^{-1}) of global NH_3 emissions (Bouwman et al., 1997).

Emissions of NO and N_2O from riparian zone soils are primarily regulated by the activity of nitrifying and denitrifying soil bacteria (Firestone et al., 1980; Tiedje et al., 1984; Anderson and Levine, 1986; Davidson et al., 1986). Studies have shown that, although NO is an in-

termediate product of both nitrification and denitrification, nitrification is the dominant source of soil NO under typical environmental conditions (Anderson and Levine, 1986). Numerous studies have shown a positive correlation between NO flux and soil N (Gasche and Papen, 1999; Russow et al., 2000), soil temperature (Slemr and Seiler, 1984; Conrad, 1996; Thornton et al., 1997; Martin et al., 1998), and, under certain conditions, soil moisture (Davidson, 1991; Valente and Thornton, 1993; Martin et al., 1998). The relative importance of nitrification and denitrification to N_2O production is difficult to discern (Rester et al., 1997; Stevens et al., 1997), however, anaerobic NO₂⁻ reduction through denitrification is considered the dominant pathway of N_2O production (Russow et al., 2000). Factors known to influence soil N_2O emission include available N, temperature, soil moisture content, and pH (Conrad, 1996). Furthermore, N_2O emissions from both riparian zones and grazed pastures generally exhibit high variability in time and space (Firestone and Davidson, 1989; Denmead et al., 2000; Groffman et al., 2000).

In general, soil NH_3 emissions will be highest in warm, neutral to alkaline soils with an adequate supply of NH_4^+ and low cation exchange capacity (Langford et al., 1992; Whitehead and Raistrick, 1993). The partial pressure of NH_3 in soil increases with concentration of NH_4^+ , pH, and temperature (Langford et al., 1992). Soils will become a source of NH_3 when the partial pressure in the soil exceeds the atmospheric NH_3 partial pressure. Soil receiving cattle urine will exhibit relatively large NH_3 losses to the atmosphere, following hydrolysis of urea to ammonium carbonate. This process proceeds rapidly and the resulting pool of NH_4^+ is depleted through NH_3 volatilization (Jarvis et al., 1989).

We quantified soil fluxes of NO, N_2O , and NH_3 as part of a project investigating water quality impacts of riparian zone restoration. Seasonal fluxes in a restored riparian zone and adjacent riparian zone grazed by cattle, measured during the first two years following restoration, are presented. System differences in relationships between flux, temperature, available N, and soil moisture are illustrated, and the impact of restoration on flux rates is assessed.

2. Methods

2.1. Site description

Fluxes were measured at a site near Dillard, Georgia (34.97° N, 83.39° W), located in the state's Blue Ridge Mountains physiographic province. Soils are Saunook series, line-loam (USDA, 1996). The receiving stream at this site is Sutton Branch, a first-order tributary of the Little Tennessee River. Historic and contemporary landuse adjacent to the stream is beef cattle grazing, and

the riparian **zone** has been severely degraded by cattle. Characteristics of riparian zones impacted by cattle overgrazing include soil compaction, lack of vegetation, chronic nutrient input, and bank **destabilization** (Belsky et al., 1999). In June 1998, as part of the Upper Little Tennessee River Comprehensive Non-point Source Management Project, cattle were excluded from a portion of the riparian zone along a 610 m section of the stream by fencing, establishing a 12 m wide buffer on each side of the stream. Hence, fencing provided an area within the riparian zone that was recovering from the impacts of cattle grazing (i.e., “restored”) and an area that was still impacted by cattle grazing (i.e., “unrestored”). Native vegetation was allowed to return, and *Salix*, *Platanus*, and *Populus* seedlings were planted at wide (>3 m) spacing.

2.2. Flux calculation

Trace gas fluxes were determined using a flow-through chamber mass balance technique (Kaplan et al., 1988; Aneja et al., 1996; Roelle et al., 1999). The chambers were transparent acrylic lined with Teflon (**polytetrafluoroethylene**) film. The cylindrical 28.2-l chamber was placed onto a stainless steel collar driven into the soil approximately 25 cm. The soil collar was inserted into the soil at least 12 h prior to placement of the chamber. Dry **zero** grade air was pumped into the chamber at a constant rate (**4.0–5.5** lpm) and drawn from the chamber at approximately 1 lpm. The excess air was vented, **minimizing** pressure differences between the chamber and the atmosphere. After the flow rate to the chamber was set, the gas concentration in the chamber was allowed to reach steady state between flux from the soil and net removal processes (NO and **NH₃**) in the chamber (**–30 min**). Only measurements taken after this transition period were used for flux calculation. Air from the chamber was drawn directly to analytical **instrumentation** for online determination of gas concentrations. The flux was determined **by** the equation:

$$J = [C]_o \left(\frac{Q}{A} + L \right) \quad (1)$$

where J is the gas flux (**ng N m^{–2} s^{–1}**), $[C]_o$ is the gas concentration (**ng m^{–3}**) at the chamber outlet, Q is the carrier gas flow rate (**l s^{–1}**), A is the soil surface ($A = 0.0794 \text{ m}^2$) enclosed by the chamber, and L (**m s^{–1}**) represents gas loss to the chamber wall per unit area (Kaplan et al., 1988). The average value of the loss term observed in the study was $L = 9.16 \times 10^{-4} \text{ m s}^{-1}$ for NO and $5.6 \times 10^{-4} \text{ m s}^{-1}$ for **NH₃**. On average, this loss accounts for approximately 50% of the total flux of both species. Given its atmospheric stability, a loss term for **N₂O** was not calculated.

Concentrations of NO and **NH₃** inside the chamber were determined using a **Thermo** Environmental In-

struments Incorporated (TEI) Model 17C **chemiluminescent NO_x/NH₃** analyzer. The basic operating principle of this instrument involves the reaction of NO with ozone (**O₃**), which produces an excited nitrogen dioxide (**NO₂**) molecule that, upon decay to a lower energy state, produces a luminescence proportional to the concentration of NO present in the sample (TEI, 2000). The concentration of **NH₃** in the sample is calculated as the difference between the total N (**Nt** = **NO** + **NO₂** + **NH₃**) and NO, (**NO** + **NO₂**) channels of the instrument. To calculate Nt, the sample is passed through an external thermal converter (825 °C) which converts **NO₂** + **NH₃** to NO. The NO from these sources is then detected in the reaction chamber, representing the concentration of Nt. Similarly, NO is converted to NO as it passes through an internal molybdenum converter (325 °C). Again, the NO from these sources is then detected in the reaction chamber, representing the concentration of NO. Ammonia concentration is then determined as **Nt–NO**. An external pump draws air through the **analyzer** at a constant rate of approximately **0.650 l min^{–1}**. Switching between the NO, Nt, and NO channels is controlled via timed solenoid valves.

The analyzer was typically operated on the 0–50 ppb scale, and was calibrated with a TEI Model 146 dynamic calibration system by mixing zero air and NO. **Multi-point** calibrations consisted of a zero point, a span value at 80% full scale, and concentrations at **70%, 50%, 30%, 20%**, and 10% of full scale to generate calibration curves for all three channels. Calibrations were performed at the beginning and end of each measurement intensive, and zero/span procedures were performed daily. The high temperature converter efficiency was determined by introducing a known concentration of **NH₃** within the range of observed **NH₃** values. The efficiency of the molybdenum NO converter was tested by introducing a known concentration of **NO₂** generated by mixing NO with **O₃**. One-minute average chamber concentrations of NO and **NH₃** were recorded continuously and averaged to yield **5-min** average fluxes.

Nitrous oxide concentrations were determined using a Hewlett Packard 5890 gas **chromatograph** with electron capture detection (Porapak Q column, 2 m length, 5 ml sample loop). The system was **configured** for continuous on-line monitoring, and the concentration of **N₂O** in the flux chamber was determined approximately every 12 min. The system was multipoint calibrated at the beginning and end of each measurement intensive as described above. All analytical and data acquisition equipment were housed in a temperature-controlled mobile laboratory.

2.3. Soil parameters

Soil temperature (averaged over 0–10 cm, Campbell Scientific probe Model 107) and volumetric water

content (averaged over 0–15 cm, Campbell Scientific Model 615 water content reflectometer) were measured continuously within the unrestored and restored riparian zones during flux measurement periods. Soil NO_3^- and NH_4^+ concentrations (0–10 cm) were determined during flux measurement periods using a Perstorp 3500 colorimetric system following the extraction and analytical methods developed by the Coweeta Hydrologic Laboratory (US Forest Service, 2000). Porous cup lysimeters (30 cm soil depth) were used to sample soil solution NO_3^- and NH_4^+ following analytical procedures developed at Coweeta Hydrologic Laboratory for sediment and water samples (US Forest Service, 2000). Lysimeters were installed at 3-m spacing from stream edge to inside the unrestored area along nine transects evenly spaced throughout the study area. After an equilibration period of 3–4 weeks, lysimeters were sampled weekly. Samples were composited and analyzed monthly.

2.4. Trace gas flux data description

Nitric oxide and NH_3 fluxes were measured approximately every three months between July 1998 and August 2000. Nitrous oxide measurements began in June 1999. Typical measurement periods lasted from 4 to 7 days. Fluxes were measured in two locations within both the restored riparian zone and the unrestored riparian zone during each measurement period. Chambers were placed in the same general area from season to season. Average fluxes consist of daytime values only. The average number of 5-min flux values in an individual measurement period was 170, 200, and 100 for NO , NH_3 , and N_2O , respectively. Unrestored and restored riparian NH_3 values for July 1998 and unrestored NH_3 values for April 1999 were omitted from the analysis due to moisture-induced sampling difficulties which resulted in flux underestimation.

2.5. Statistical analysis

In this study, differences in means were tested for statistical significance using the non-parametric Wilcoxon rank sums test. This test is robust with respect to

outliers and does not assume that the sample is drawn from a particular theoretical distribution (Schlotzhauer and Littell, 1987). The relationships between trace gas fluxes and soil temperature, moisture, and N concentrations were examined using regression analysis. Models were fit using the method of least squares (SAS, 1992). All analyses were performed using SAS statistical software.

3. Results and discussion

3.1. Fluxes

Overall, fluxes were slightly larger in the unrestored riparian zone than the restored riparian zone for all three gases (Table 1). Also, total flux variance was larger in the unrestored riparian zone for all species, though variation was substantial in both the restored and unrestored areas (Table 1). On average, replicate mean NO , NH_3 , and N_2O fluxes differed by 70%, 90%, and 6%, respectively, within the restored riparian zone during individual measurement periods. Replicate means within the unrestored riparian zone varied by 110%, 143%, and 32%, respectively, during individual measurement periods. Larger spatial variation in the unrestored riparian zone was likely due to more spatially heterogeneous patterns of soil compaction, vegetation disturbance, and N input due to cattle grazing.

3.1.1. Ammonia

There was considerable temporal variation in NH_3 flux for both unrestored and restored riparian zone measurements (Fig. 1a). Except during August 1999 and February 2000, differences between unrestored and restored riparian zone NH_3 fluxes were statistically significant ($p < 0.10$). Edaphic factors regulating this temporal variation were difficult to discern in either the unrestored or restored riparian zone. Results from linear regression analyses indicated no statistically significant ($p > 0.10$) relationship between temporal variation in NH_3 flux and either soil temperature or moisture. Average soil temperature (0–10 cm) within the restored

Table 1
Summary flux ($\text{ng N m}^{-2} \text{ s}^{-1}$) statistics for the unrestored and restored riparian zones

Gas	Location	N	Mean ($\text{ng N m}^{-2} \text{ s}^{-1}$)	Standard deviation	Minimum	Maximum
NO	Unrestored	8	9.1	11.5	0.7	33.1
NO	Restored	8	5.8	4.0	1.8	12.2
NH_3	Unrestored	6	4.3	6.2	0.3	15.8
NH_3	Restored	7	2.0	1.9	0.2	6.0
N_2O	unrestored	5	77.7	92.1	0.0	182.0
N_2O	Restored	5	76.7	84.8	0.0	200.3

Means consist of daytime (7:00 AM–8:00 PM) 5-min average fluxes averaged by seasonal measurement period.

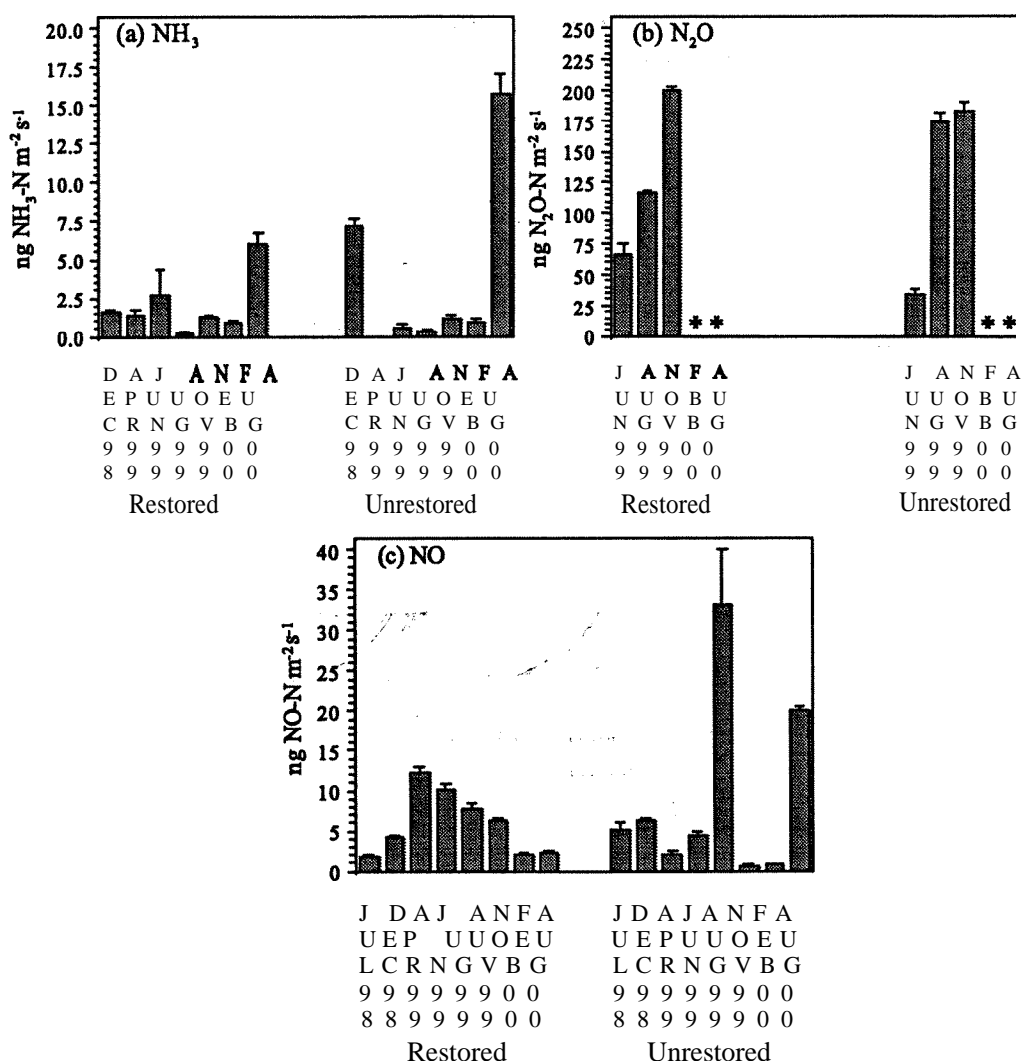


Fig. 1. Fluxes ($\text{ng N m}^{-2}\text{s}^{-1}$) averaged by measurement period within the **unrestored** and **restored** riparian zones. Bar extensions represent the upper 95% confidence limit for the mean. Asterisks during February and August 2000 in the N_2O chart represent average fluxes below detection limit.

riparian zone during seasonal measurement periods ranged from 9.7 to 26.1 °C. Throughout the study, soil volumetric water in the restored riparian zone (0–15 cm) ranged from 18.2% to 46%, while averaging 34.3%. Saturation volumetric water content was approximately 64% in the restored riparian zone after reversal of compaction.

In the restored riparian zone, flux was not correlated ($p > 0.10$) with soil NO_3^- or NH_4^+ concentrations but was highly correlated with the ratio of NH_4^+ to NO_3^- ($R^2 = 0.84$, $p = 0.007$). Studies have shown that observed spatial patterns of NH_4^+ concentration in restored riparian soils may be partly related to patterns of dissimilatory NO_3^- reduction to NH_4^+ (DNRA; Schipper et al., 1994). In soils that contain low NO_3^- -to-carbon (C) ratios, anaerobic NO_3^- reduction may be primarily

controlled by DNRA rather than **denitrification**, which may dominate when NO_3^- -to-C ratios are high (Tiedje et al., 1982; Tiedje, 1988). Schipper et al. (1994) observed lowest soil NH_4^+ concentrations at the **upslope** edge of the riparian zone where NO_3^- concentrations and **denitrifying** enzyme activity (DEA) were highest and maximum NH_4^+ concentrations near the stream where DEA was lowest. In the present study, we also observed decreasing soil solution NO_3^- concentrations (30 cm lysimeters) from the edge of the restored riparian zone to the stream coupled with increasing NH_4^+ concentrations (Fig. 2). At this site, soil within the restored **riparian** zone exhibits relatively low %N-to-%C ratios (%N:%C < 0.1, 0–30 cm). The observed relationship between NH_3 loss to the atmosphere and NH_4^+ -to- NO_3^- ratio in this study suggests that NH_3 loss may be greater

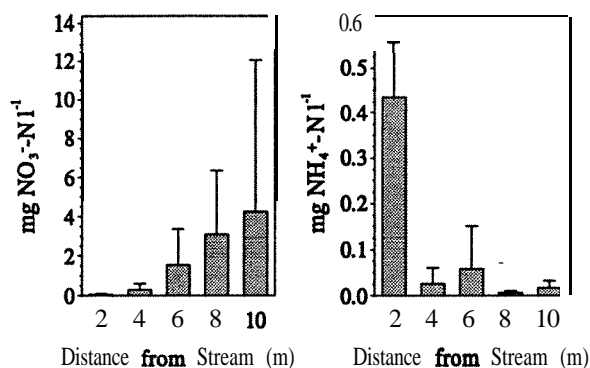


Fig. 2. Average 30 cm lysimeter $\text{NO}_3\text{-N}$ and $\text{NH}_4^+\text{-N}$ concentrations (mg l^{-1}) vs. distance from stream (m) within the restored riparian zone. Bar extensions represent the upper 95% confidence limit for the mean. Note the difference in scales between charts.

where the $\text{NH}_4^+\text{-to-NO}_3^-$ ratio is high, signifying a readily available, new pool of NH_4^+ . As illustrated in Fig. 2, spatial variability in soil $\text{NH}_4^+\text{-to-NO}_3^-$ ratio, and thus NH_3 loss to the atmosphere at this site, may be at least partially controlled by partitioning of NO_3^- reduction between DNRA and denitrification and variation in the environmental controls which regulate the corresponding microbial activity of those mechanisms. Following this hypothesis, Fig. 2 also reflects the importance of measuring fluxes along a gradient from the restoration boundary to the stream. In this study, however, fluxes inside the restored riparian zone were consistently measured approximately 2.5 m from the restoration boundary.

In the unrestored riparian zone, statistical relationships between measurement period average NH_3 flux and soil temperature, moisture, and N concentrations were not significant ($p > 0.10$). Given the irregular presence of cattle in the unrestored riparian zone and associated variability in N inputs, vegetation disturbance, and compaction, the absence of clear relationships between flux and edaphic factors is not surprising. It is possible that the variation in average NH_3 fluxes may be more readily explained by spatial variation in cation exchange capacity or spatiotemporal variation in pH, variables which were not quantified in this study. Overall, the fluxes observed in this study are similar to fluxes measured by Roelle and Aneja (2002) in a fallow agricultural soil ($3.4\text{--}26.1 \text{ ng NH}_3\text{-N m}^{-2} \text{ s}^{-1}$) using the dynamic chamber technique.

3.1.2. Nitrous oxide

Excluding February and August 2000, when N_2O fluxes were below detection limits, differences between restored and unrestored riparian zone measurement period means were statistically significant ($p < 0.10$) and large temporal variability was observed in both the un-

restored and restored sections of the riparian zone (Fig. 1b). During February 2000, average soil temperature (0–10 cm) was 8.5°C , which would likely reduce microbial activity. During August 2000, soil volumetric water was 36% and 18% in the unrestored and restored sections of the riparian zone, respectively. Under these moisture conditions, the soil is likely to be mostly aerobic. Anaerobic bacteria responsible for N_2O production through denitrification would therefore be minimally active.

In the restored riparian zone, average fluxes were positively correlated with soil NO_3^- concentration ($R^2 = 0.83$, $p = 0.02$). Because N_2O is a product of both the formation and reduction of NO_3^- , this correlation does not indicate whether nitrification or denitrification was the source of N_2O . This does suggest, however, that the near-surface soil was active in processing N entering the restored riparian zone. Relationships between restored riparian N_2O flux, temperature, and soil moisture were not evident ($p > 0.10$). If flux was NO_3^- limited, the influence of soil moisture and temperature on flux may have been negligible. In the unrestored riparian zone, statistical relationships between average flux and soil temperature, moisture, and N concentrations were not evident ($p > 0.10$). Cattle-induced variability in soil conditions may have confounded such relationships.

Since riparian zones have been shown to process significant amounts of NO_3^- in groundwater, it has recently been hypothesized that these systems may represent “hotspots” of N_2O emissions to the atmosphere (Groffman et al., 1998, 2000). While numerous studies have addressed the issue of denitrification in riparian soils (see Martin et al., 1999), relatively few studies have addressed the issue of N_2O production in groundwater (see Groffman et al., 2000). Measurements of N_2O emissions from riparian soils are even more limited, though Weller et al. (1994) published a dataset containing N_2O emissions from a forested riparian zone receiving runoff from an adjacent cornfield. At that site, groundwater NO_3^- concentrations were shown to decrease from 2–10 to $<1 \text{ mg NO}_3\text{-N l}^{-1}$ during transit through the riparian zone (Weller et al., 1994). Fluxes measured in that study were much lower ($1.5\text{--}2.8 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$) than the fluxes observed in the present study. This difference may be attributed to a number of factors. For example, Weller et al. (1994) may have observed conditions which favor a predominance of N_2 rather than N_2O production during denitrification (Groffman et al., 2000). Weller et al. (1994) also reported relatively low concentrations of N_2O in groundwater during that study. The fluxes observed in our study (24.2 and $24.5 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$) are within the range of fluxes ($0\text{--}41.8 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$) for mineral agricultural soils reported in a review by Bouwman (1996). Our results are similar to those of Weller et al. (1994), however, in that while both study sites show a reduction

in groundwater NO; from the riparian zone boundary to the stream, N_2O emissions are not, on average, highest at the measurement location nearest the stream. Weller et al. (1994) attributed this to large spatial variability in denitrification rates and the factors controlling the ratio of N_2 to N_2O .

3.1.3. Nitric oxide

The temporal pattern of NO flux in the restored riparian zone was much different than flux in the un-restored riparian zone (Fig. 1c). During all periods, restored and un-restored riparian zone mean fluxes were significantly different ($p < 0.10$). In the restored riparian zone, flux increased $\approx 600\%$ ($1.8\text{--}12.2 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$) during the first year following restoration. During the second year, flux decreased to levels observed at the onset of restoration ($1.6 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$). In contrast, flux within the un-restored riparian zone did not display this temporal pattern.

Average NO flux within the restored riparian zone was positively correlated with soil NH_4^+ concentration ($R^2 = 0.87$, $p = 0.005$). As previously mentioned, NH_4^+ is necessary for nitrification to proceed. Soil temperature, moisture, and NO; concentration were not significant explanatory variables ($p > 0.10$). In the un-restored riparian zone, NO flux was positively correlated with soil temperature ($R^2 = 0.29$, $p = 0.098$) and NO; concentration ($R^2 = 0.67$, $p = 0.030$). Nitrate is a product of nitrification and is the substrate necessary for denitrification. Though NO is a byproduct of both processes, the different relationships between NO flux and soil N in the restored and un-restored areas is characteristic of differences in microbial characteristics within the two soils.

The pattern of NO flux in the restored riparian zone was likely the cumulative result of physical, chemical, and biological factors. The flux increase during the first year following restoration is consistent with the observed decrease in bulk density ($1.15\text{--}0.95 \text{ g cm}^{-3}$), which likely resulted in increased soil aeration. This increased aeration may have increased the activity of aerobic nitrifying bacteria, thereby stimulating NO emissions. The observed relationship between NO flux and soil NH_4^+ concentration indicates that nitrification may be the primary source of NO in the restored riparian zone. The average NO flux values observed in this study are similar to flux magnitudes for other agricultural soils in the southeast US ($1.0\text{--}7.0 \text{ ng NO-N m}^{-2} \text{ s}^{-1}$; Aneja et al., 1996).

3.2. Riparian nitrogen cycling

We have shown that flux magnitudes were slightly larger in the un-restored riparian zone. A relevant question is whether or not restoration increased or decreased the importance of trace gas emission as a pathway of N diversion from the receiving stream. Table 2 shows ratios of flux ($\text{ng N m}^{-2} \text{ s}^{-1}$) to soil N [$(\text{NH}_4^+-\text{N}) + (\text{NO}_3^--\text{N})$]

Table 2

Ratio of flux ($\text{ng N m}^{-2} \text{ s}^{-1}$) to soil N [$(\text{NH}_4^+-\text{N}) + (\text{NO}_3^--\text{N})$] within the restored and un-restored riparian zones

Ratio	Restored	Unrestored
NO flux/soil N ^a	3.18	1.74
NH_3 flux/soil N	3.27	1.21
N_2O flux/soil N	28.6	27.7

^a $\text{ng NO-N m}^{-2} \text{ s}^{-1} / \text{mg N kg soil}^{-1}$, where soil N = $(\text{NH}_4^+-\text{N}) + (\text{NO}_3^--\text{N})$.

within the restored and un-restored sections of the riparian zone for NO, NH_3 , and N_2O . Ratios of NO and NH_3 flux to soil N were 1.45 and 2.1 times larger, respectively, in the restored riparian zone. This indicates that the restored riparian zone was more efficient than the un-restored riparian zone in exporting N from the soil to the atmosphere and that restoration, therefore, improved the ability of surface soils to divert N from the receiving stream, particularly through emissions of NO and NH_3 .

Average soil NH_4^+-N concentrations (0–10 cm) in the restored riparian zone experienced a net decrease ($\approx 95\%$) from 5.11 to $0.33 \text{ mg NH}_4^+-\text{N kg}^{-1}$ (Fig. 3, $R^2 = 0.77$, $p < 0.001$) over the period April 1999–August

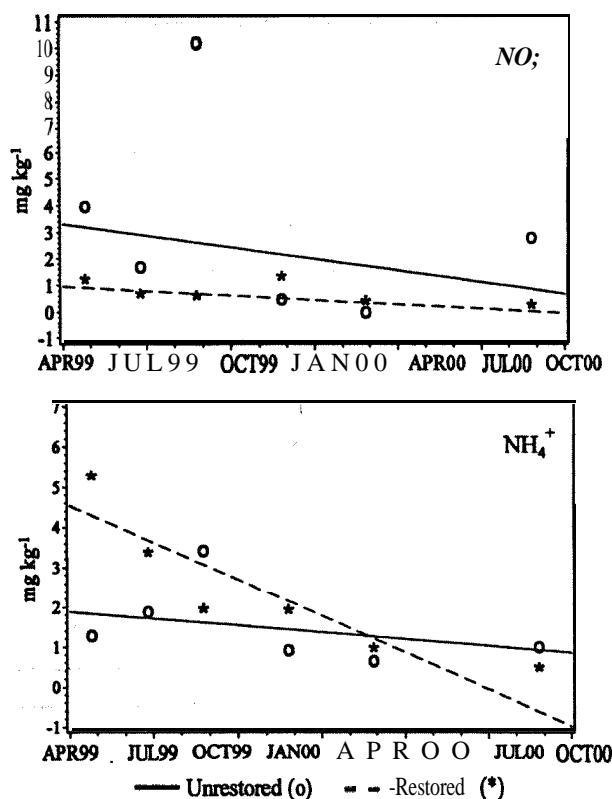


Fig. 3. Soil (0–10 cm) NH_4^+-N and NO_3^--N concentrations (mg kg^{-1}) within the un-restored and restored riparian zones. Symbols represent mean values. Regression lines were fit to all data points. Note the difference in scales between charts.

2000, corresponding to an 87% decrease in NO flux. Average soil NO_3^- -N concentrations (0-10 cm) in the restored riparian zone experienced a net decrease from 0.98 to 0.02 mg NO_3^- -N kg^{-1} ($R^2 = 0.29$, $p = 0.032$) over the same period. Concentrations of NH_4^+ -N ($p = 0.47$) and NO_3^- -N ($p = 0.32$) in the unrestored area did not exhibit statistically significant trends (Fig. 3). In the restored riparian zone, concentrations at the end of the period are lower than those reported for forest soils (3.1-4.6 mg NH_4^+ kg^{-1} , 1.2-1.6 mg NO_3^- kg^{-1}) in this region (Waide et al., 1988). This suggests that residual N in the upper 10 cm of soil was quickly processed following restoration, and that new N input from the unrestored riparian zone is either efficiently processed within, or quickly transported through, this layer. This response in soil N concentrations likely results from increased accumulation in vegetation and increased N processing efficiency and/or increased biomass of soil microbes. The observed increase in NO flux during the first year following restoration and higher efficiency of the restored riparian zone in converting N to NO and NH_3 gases, is consistent with this response.

4. Conclusions

Seasonal measurements of NO, NH_3 , and N_2O trace gas fluxes during the first two years following restoration of a degraded riparian zone are presented, along with fluxes from the adjacent unrestored section of the riparian zone. In the restored riparian zone, average NO, NH_3 , and N_2O fluxes were 1.83, 0.63, and 24.19 kg N $\text{ha}^{-1} \text{y}^{-1}$, respectively. Fluxes in the unrestored riparian zone were slightly higher, measuring 2.87, 1.35, and 24.50 kg N $\text{ha}^{-1} \text{y}^{-1}$ for NO, NH_3 , and N_2O , respectively. Nitrous oxide flux was most important in terms of N loss from the restored riparian zone, followed by NO and NH_3 .

Variability in restored riparian seasonal average fluxes was explained by variability in soil N concentrations. Nitric oxide flux was positively correlated with soil NH_4^+ concentration, while N_2O flux was positively correlated with soil NO_3^- concentration. Ammonia flux was positively correlated with the ratio of NH_4^+ to NO_3^- . Relationships between NH_3 flux, soil temperature, and moisture were not evident. In the unrestored riparian zone, average NH_3 , and N_2O fluxes were not explained by soil temperature, N concentrations, or moisture. This is likely due to high variability in soil conditions related to cattle effects, such as compaction and N input. Nitric oxide flux in the unrestored riparian zone was positively correlated with soil temperature and NO_3^- concentration. Restoration appeared to significantly affect NO flux, which increased $\approx 600\%$ during the first year following restoration and, during the second year, decreased to levels encountered at the onset of restoration.

Two years following restoration, it does not appear that this landuse change has altered N trace gas emission in a way that would impact regional budgets of NO, NH_3 , and N_2O , given large-scale implementation of riparian restoration measures. Our results do show, however, that NO flux increased significantly during the first year following restoration before returning to pre-restoration levels. Also, observed N_2O fluxes are higher than previously published measurements for riparian zones. By comparing the ratio of total trace gas flux to soil N concentration, we show that the restored riparian zone was more efficient than the grazed riparian zone at diverting surface soil N from the receiving stream to the atmosphere.

It is likely that the impact of restoration on N trace gas emissions is highly site specific. For example, Groffman et al. (2000) point out that the impact of riparian restoration on N_2O emissions depends on the ratio of N_2O to N_2 produced during denitrification, which is regulated by soil pH, NO_3^- concentration, and denitrification rate (Groffman et al., 2000). To accurately assess the potential impact of riparian restoration on regional or national NO, NH_3 , and N_2O budgets, flux measurements must accurately reflect at least watershed-scale variability. Fluxes will vary with site characteristics such as soil type, vegetation type, magnitude and speciation of N input, and hydrologic characteristics.

During this study, we observed large spatial and temporal flux variability within both the restored and unrestored sections of the riparian zone. This indicates that we should make more than two replicate measurements in space per treatment per measurement period in future experiments. We recommend a combination of replicate measurements spaced systematically with respect to the stream and a large chamber footprint to appropriately capture spatial flux variability.

We believe that the high degree of variability observed in fluxes and soil N concentrations was primarily due to the irregularity of cattle activity in the unrestored riparian zone, and that this variability and lack of microbiological information significantly limited our ability to examine N cycling processes at the mechanistic level. In order to extend the work presented here to investigate the N cycling mechanisms in restored riparian zones, we have implemented controlled experiments at a second site. Our intent during this second phase of the project is to identify and characterize the primary physical, chemical, and biological mechanisms regulating nutrient transport and transformation within both currently degraded and restored riparian zones previously degraded by cattle.

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